

PCT

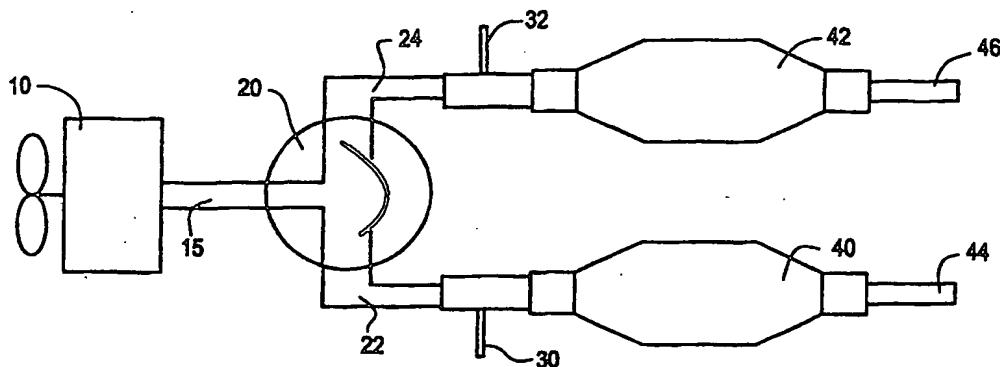
WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

BM

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : F01N 3/08, B01D 53/94	A1	(11) International Publication Number: WO 98/45582 (43) International Publication Date: 15 October 1998 (15.10.98)
(21) International Application Number: PCT/US98/05536		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).
(22) International Filing Date: 19 March 1998 (19.03.98)		
(30) Priority Data: 08/833,700 8 April 1997 (08.04.97) US		
(71) Applicant: ENGELHARD CORPORATION [US/US]; 101 Wood Avenue, P.O. Box 770, Iselin, NJ 08830-0770 (US).		
(72) Inventors: DEEBA, Michel; 2501 North Oaks Boulevard, North Brunswick, NJ 08902 (US). HOCHMUTH, John, K.; 32 Tunison Lane, Bridgewater, NJ 08807 (US).		
(74) Agents: MILLER, Stephen, I. et al.; Engelhard Corporation, 101 Wood Avenue, P.O. Box 770, Iselin, NJ 08830-0770 (US).		

(54) Title: APPARATUS, METHOD, AND SYSTEM FOR CONCENTRATING ADSORBABLE POLLUTANTS AND ABATEMENT THEREOF



(57) Abstract

A new method, system, an apparatus are described for the adsorption and concentration of adsorbable pollutants. The invention allows for simultaneous pollutant adsorption and pollutant concentration. The invention is particularly useful in treating the exhaust of internal combustion engines containing adsorbable pollutants which can be concentrated and then treated to form harmless effluents. The flow of exhaust gas is divided into two streams which are directed to two parallel adsorption means (42, 40), the first one in adsorption phase and the second one in regeneration.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	VN	Viet Nam
CF	Central African Republic	JP	Japan	NL	Netherlands	YU	Yugoslavia
CG	Congo	KE	Kenya	NO	Norway	ZW	Zimbabwe
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand		
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		

- 1 -

**APPARATUS, METHOD, AND SYSTEM FOR CONCENTRATING
ADSORBABLE POLLUTANTS AND ABATEMENT THEREOF**

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention is broadly concerned with abatement of pollutants, particularly with adsorbable pollutant concentration in gaseous streams. More specifically, the present invention is concerned with a novel apparatus, method, and system for concentrating adsorbable pollutants (such as NO_x and SO_x) present in the exhaust stream of internal combustion engines (gasoline or diesel) comprising at least two adsorbable pollutant adsorption means (trapping materials) capable of operating simultaneously and in parallel to adsorb and concentrate the pollutants. The concentrated pollutants then may be further treated to form non-polluting effluents.

2. Related Art

It is well known in the art of internal combustion engine exhaust treatment to utilize catalyst compositions such as those commonly referred to as three way conversion (TWC) catalysts. Such catalysts have been found to successfully promote both oxidation of unburned hydrocarbons (HC) and carbon monoxide (CO) and the reduction of NO_x in the exhaust gas, provided that the engine is operated at or close to stoichiometric air/fuel conditions. However, many present day engines,

- 2 -

especially gasoline-fueled engines used for passenger automobiles and the like, are designed not to operate at stoichiometric air/fuel conditions at least part of time as a fuel economy measure. In such lean-operating
5 engines, the ratio of air to fuel in the combustion mixture supplied to the engine is maintained above the stoichiometric ratio so that the resulting exhaust gases are "lean", i.e., the exhaust gases are relatively high in oxygen (5-10% O₂) content and relatively low in
10 reductants content, e.g., HC, CO, and/or hydrogen.

Although lean-burn engines provide enhanced fuel economy, a disadvantage is that conventional TWC catalysts cannot adequately abate the NOx component of the pollutants in the gas stream because high NOx
15 conversion rates require reductant-rich conditions. The art has devoted great effort to treat the exhaust of lean-burn engines. The best catalysts known to abate NOx from engines under lean-burn conditions are those containing platinum. However, these catalysts have
20 limitations of only reducing about 20 to 40% of the NOx in the exhaust mainly to N₂O over a relatively narrow temperature range of 200-275°C. Another disadvantage of such catalysts is the high oxidation activity of SO₂ to sulfate under lean-burn conditions.

25 Other efforts to reduce NOx in lean-burn engines include combinations of TWC catalyst systems with NOx traps (sorbent materials). The NOx traps contain sorbent materials capable of adsorbing or "trapping" oxides of nitrogen and sulfur under lean conditions. The trapped

- 3 -

oxides are desorbed and reduced under fuel-rich conditions thereby regenerating the traps. Therefore, it has been proposed that these so called NO_x traps be utilized in what is called a "partial lean-burn" operating strategy. Here, the vehicle operates lean under some driving conditions and is controlled at the stoichiometric air-to-fuel (A/F or λ) ratio under other driving conditions. While operating lean, the engine is periodically subjected to rich fuel or reductant spikes to desorb and reduce NO_x and regenerate the trapping function. The problem with this operating mode is that the vehicle cannot take full advantage of the fuel economy gains obtained under full-lean burn operating conditions because the engine operates lean only a fraction of the time. In addition, the rich spikes result in significant fuel economy losses because a significant amount of reductant is required to create a rich condition in the exhaust. Therefore, the gains obtained from the lean operating modes are less than 100%.

US Patent No. 5,365,734 to Takeshima discloses an apparatus having at least two lean NO_x catalysts installed in parallel in the exhaust gas system of an internal combustion engine. The apparatus has means for changing the space velocity of the exhaust gas to each of the catalysts such that when the space velocity through one catalyst is high, the space velocity through the other catalyst is low. It is stated that by alternating the exhaust gas between high and low space velocities

- 4 -

across the NO_x catalyst, improved NO_x catalysis is achievable. The NO_x catalyst is said to be an ion-exchanged transition metal/zeolite catalyst. Examples of transition metals given are copper and cobalt. However, 5 the patent is silent with regards to means for adsorbing adsorbable pollutants such as NO_x and SO_x to provide a concentrated pollutant-containing stream.

The present invention provides an advance over the related art by providing a novel adsorbable pollutant 10 concentration solution as described herein.

SUMMARY OF THE INVENTION

The present invention provides an apparatus, method, and system for adsorbable pollutant concentration. The apparatus comprises:

- 15 (a) an inlet conduit for receiving gases containing adsorbable pollutants;
- (b) means for separating and controlling the gases from said inlet conduit between at least a first conduit and a second conduit;
- 20 (c) a first pollutant adsorption means in fluid communication with said first conduit, said first means having inlet and outlet conduits; and
- (d) a second pollutant adsorption means in fluid communication with said second conduit, said second means having inlet and outlet conduits.

Further embodiments of the apparatus include combining the adsorption means with catalytic means for

- 5 -

further treatment of the adsorbable pollutants and other pollutants that may be present.

In practicing the method and system of the present invention, the pollutant adsorption means cycle between a high-flow, adsorbing (trapping) mode and a low-flow, concentration (regeneration) mode. The amount of exhaust gas flowing to each of the adsorption means is controlled by separator means. The separator means is not required to close and thus provides means to continuously adsorb and concentrate the pollutants from the exhaust gas.

Relative amounts of gas flow in the high-flow mode and the low-flow mode are discussed further herein. At some point in time during the low-flow condition, adsorbed pollutants are released from the adsorbent to form a concentrated pollutant-containing stream. In the embodiment where the adsorbable pollutant is NO_x and the adsorbent is full, fuel reductant is added to the exhaust flow to produce a rich air-to-fuel (A/F) ratio at the NO_x adsorbent thereby regenerating the adsorbing function.

It is important to note that the addition of reductant may not be required over the entire duration of the low-flow condition. That is, reductant is added only during the low-flow (regeneration) mode to change the A/F ratio of the regeneration flow from lean to rich.

Some of the advantages of the present invention when applied to gasoline or diesel engine operation are:

1. The engine can operate lean at all driving conditions to take complete advantage of lean fuel economy gains.

- 6 -

2. The injection of fuel to regenerate the trap is only a small volume of that required compared with other known lean-burn modes where fuel is injected into the full air or exhaust flow of the engine.

5 3. This invention is complemented from the use of conventional TWC catalysts for abating NOx and other pollutants. TWC catalysts are well developed and can give more than 90% NOx conversion to N₂.

10 4. The use of a separator means that allows different proportions of exhaust to pass through either of the adsorption means has great economical benefits. One major benefit is that the gas being used in the regeneration cycle is significantly lower in oxygen content (5-7%) than ambient air (21%) and thus requires 15 less fuel to transform the gas from a lean to rich condition in order to accomplish regeneration of the adsorption means.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows one embodiment of this invention's
20 apparatus.

Figure 2 shows a second embodiment, of this invention containing various sensor and control means.

Figure 3 depicts a generalized algorithm for controlling the apparatus of the invention.

25 Figure 4 illustrates the bench scale apparatus used to simulate the invention.

Figure 5 illustrates NOx conversion for comparative example, C-1.

- 7 -

Figure 6 illustrates NOx conversion for comparative example, C-2.

Figure 7 illustrates NOx conversion for inventive example, I-1.

5 Figure 8 illustrates NOx conversion for inventive example, I-2.

Figure 9 illustrates NOx conversion for inventive example, I-3.

10 Figure 10 illustrates NOx conversion for inventive example, I-4.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The apparatus, method, and system of the present invention relate to improved pollutant abatement systems. The present invention will become apparent from the 15 following definitions and by reference to the accompanying figures.

For purposes of this invention, adsorbable pollutants are pollutants capable of being adsorbed onto a sorbent material. Examples of such pollutants are NOx (predominantly nitric oxide and nitrogen dioxide), and SOx (predominately sulfur dioxide and sulfur trioxide).

The following are definitions of terms useful in understanding the present invention:

Stoichiometric ratio - The mass of air (or oxygen) required to completely burn a unit mass of fuel to carbon dioxide and water with no oxygen left over.

Lean-burn condition - A condition where the amount of air (or oxygen) is greater than the stoichiometric ratio.

Rich-burn condition - A condition where the amount of air (or oxygen) is less than the stoichiometric amount.

Lambda Ratio (λ) - The ratio of the actual air-to-fuel (A/F) ratio to the stoichiometric air-to-fuel ratio.

5 When $\lambda > 1$, this refers to a lean condition, when $\lambda < 1$, this refers to a rich condition.

Also the terms "adsorbable", "adsorbent", "adsorption", etc., are intended to encompass both adsorption and absorption as these terms are generally 10 known to persons skilled in the art.

Figure 1 shows a preferred embodiment of the present invention in conjunction with the exhaust conduit 15 of an engine 10. The conduit 15 connects to a means for separating 20 conduit 15 into conduit 22 and conduit 24. 15 Conduit 22 enters a first means for pollutant adsorption 40. First pollutant adsorption means 40 contains an outlet conduit 44 and means for injecting a reductant 30. Conduit 24 enters a second means for pollution adsorption 42. Second pollutant adsorption means 42 contains an outlet conduit 46 and means for injecting a reductant 32. It should be noted that the reductant injection means 30 and 32 are optional as reductant can enter the apparatus by other means such as through modification of engine 10 operation to temporarily provide a rich fuel spike to 25 facilitate desorption of the pollutant in pollutant adsorption means 40 and 42. Alternately, desorption may occur through use of heating source capable of raising the adsorbent material in the adsorption means to a temperature hot enough to facilitate desorption of the

- 9 -

pollutant. Such a heating source may comprise a heating element or comprise the heat generated from the combustion of a fuel. An example of a useful heating element is one typically used for heating catalysts,
5 i.e., an electrically heated catalyst (EHC), which may conveniently be embedded in the adsorbent material.

It should be noted that in some instances it may be necessary to heat the adsorbent material to a minimum temperature sufficient to activate the adsorbency
10 function of the adsorbent material. In such instances, the heating source whether an electrical heating element or heat generated by fuel combustion may be used to heat the adsorbent bed to the necessary temperature.

Separating means 20 can comprise any number of
15 devices capable of dividing the exhaust gas in conduit 15 into conduit 22 and conduit 24. Such devices include but are not limited to valves, flaps, orifices, and the like. A key feature of separating means is its ability to conveniently operate the adsorption of the adsorbable
20 pollutant in one of the pollutant adsorption means (40 or 42) while also providing a means to regenerate the sorption material that already contains adsorbed pollutants in the other of the pollutant adsorption means (40 or 42). That is to say that while one of the
25 pollutant adsorption means is being used to adsorb, for example, NO_x or SO_x, the other pollutant adsorption means is being regenerated.

In operation, separating means 20 divides the exhaust gas flow into a high-flow stream and a low-flow

- 10 -

stream. The high-flow stream of the exhaust gas passes into one of the adsorption means for the adsorption of the pollutant. The low-flow stream of the exhaust gas passes into the other adsorption means for the 5 regeneration mode. In the low-flow mode, a stoichiometric-rich condition is created by injection of a reductant to desorb the adsorbed pollutant forming a concentrated pollutant stream. Alternately, desorption and concentration of the pollutant in the low-flow mode 10 is accomplished through use of a heating element in the adsorbent bed or through the heat of combustion of a fuel. Typically, the pollutant is desorbed when the adsorbent bed temperature reaches a temperature ranging from 400 to 800°C to desorb NOx and ranging from 500 to 15 900°C to desorb SOx.

Characteristically, separating means 20 should have a mechanism capable of alternating the high-flow condition and low-flow condition between pollutant adsorptive means 40 and 42. These mechanisms are known in 20 the art and can be any simple controlling mechanism such as an electrically, hydraulically, or pneumatically (i.e., by positive pressure or by vacuum) activated solenoid.

The pollutant adsorption means 40 and 42 comprise an 25 adsorption material. Other embodiments include adsorption means in combination with any suitable pollutant destroying catalyst system. A variety of arrangements of the catalyst and adsorption material can exist. Such arrangements include but are not limited to

- 11 -

combinations of an adsorption material with a catalyst as an overlayer or as a separate catalyst behind the adsorption materials. Other arrangements include a catalyst with an adsorptive material as an overlayer or a 5 homogeneous mixture of the adsorption material and catalyst.

Suitable adsorption materials include but are not limited to metal oxides, metal carbonates, metal hydroxides, and mixed metal oxides.

10 Suitable metals for the oxides, carbonates, and hydroxides include but are not limited to Group IA and Group IIA metals. Preferred of these metals are lithium, sodium, potassium, cesium, magnesium, calcium, strontium, and barium; most preferred are lithium, barium, and 15 strontium. Other preferred metals are lanthanum and manganese.

Examples of useful metal oxides are strontium oxide (SrO), barium oxide (BaO), calcium oxide (CaO), cesium oxide (Cs_2O), lithium oxide (LiO), lanthanum oxide 20 (La_2O_3), potassium oxide (K_2O), magnesium oxide (MgO), manganese oxide (MnO_2), and sodium oxide (Na_2O). Preferred are MnO_2 , BaO , and SrO .

Examples of useful mixed oxides are BaTiO_3 , BaZrO_3 , LaZrO_2 , MnO , LaMnO_x (where x' is an integer from 2 to 4) 25 and perovskite and spinal type mixed oxides. Also useful are mixed oxides containing La_2O_3 , CeO_2 with metal oxides such as TiO_2 , ZrO_2 , MnO_2 , BaO , and SrO . Preferred mixed oxides are those containing ZrO_2 , MnO_2 , BaO , and SrO .

- 12 -

The adsorption capabilities of the foregoing adsorbent materials may be enhanced for certain pollutants by incorporating certain metals such as precious metals. A preferred metal is platinum (Pt).

5 The adsorption enhancing amount of the precious metal is any amount capable of enhancing or promoting adsorption of the pollutant on the adsorbent material. Typically, such amounts range from 5 to 150 g/ft³, preferably from 20 to 100 g/ft³.

10 Suitable catalyst systems include but are not limited to Pt, palladium (Pd), rhodium (Rh) and combinations thereof. Preferred are Pt, Pd, Pt/Rh mixtures and Pt/Pd/Rh mixtures, most preferred are Pt/Rh mixtures and Pt/Pd/Rh mixtures.

15 Reductant injection means 30 and 32 comprises any suitable device capable of homogeneously injecting a reductant species into streams 22 and 24.

Figure 2 illustrates the apparatus of Figure 1 further comprising oxygen sensors 23 and 25, NOx sensors 20 43 and 45, and a central processing unit (CPU) 50. CPU 50 is capable of receiving signals from the various sensors, processing them, and accordingly controlling the operation of separator means 20 and reductant injector means 30 and 32.

25 As will be apparent to one skilled in the art, the control of separator means 20 and injector means 30 and 32 can be achieved with all, some, or none of the signals generated by the various sensors. For example, control of separator means 20 and injector means 30 and 32 can be

- 13 -

accomplished simply by a timer incorporated in CPU 50. In such a scenario, separator means 20 would be actuated to control the flow of gas exhaust 15 into streams 22 and 24 based on a pre-set timing sequence. The amount of 5 reductant entering through injector means 30 and 32 may also be actuated through the timer. The operation of the timer would be based on such items as engine mapping and the estimated time it would take to effectively adsorb the estimated amount of NOx in the exhaust and regenerate 10 the sorbent material. Furthermore, the timer could also be programmed to operate as a function of exhaust gas temperature and exhaust gas throughput.

For example, the amount of adsorbed NOx could be estimated from the engine air flow sensor coupled with 15 previously developed engine maps for NOx content. When the estimated amount of absorbed NOx reaches a certain level, the flow rate can be decreased and a suitable amount of reductant injected to regenerate the trapping material and reduce the NOx to N₂.

20 Somewhat more sophisticated strategies may be used to control operation of the present invention through use of the various sensors. Examples of two control strategies follow the discussion explaining a typical detailed operating cycle of the present invention.

25 Typical Cycle for concentrating and abating pollutants in engine exhaust

The main exhaust gas pollutants entering the apparatus are HC, CO, and NOx. In the high-flow

- 14 -

(adsorption) mode, approximately 51-99%, preferably 70-99%, most preferably 80-99% of the exhaust gas is directed by a valve or other appropriate separating means into a first adsorption means which contains a suitable 5 adsorption material / TWC catalyst system. The amount of the HC and CO are abated at lean conditions by the TWC catalyst to give CO₂ and water. The NOx, on the other hand, is adsorbed by the trap. Simultaneously, while the first abatement means is in the high-flow mode, the 10 remaining portion of the exhaust gas is directed to a second adsorption means containing a suitable adsorption material / TWC catalyst system. During this low-flow condition, the adsorption means is regenerated by injecting fuel in front of the adsorption means to change 15 the air-to-fuel ratio from lean to rich. At rich conditions, the NOx is released and is reduced by the TWC catalyst. After a certain preset time (or as indicated by the NOx sensor or other appropriate control means), the valve switches the high-flow exhaust gas condition to 20 the second adsorption means where HC and CO are abated and NOx is trapped.

Simultaneously, the first abatement means is regenerated in the low-flow condition. Thus, NOx is continuously adsorbed in one of the adsorption means 25 while adsorbed NOx is desorbed in the other adsorption means. The cycling strategy between the first and second adsorption means continues successively by operating the valve to provide purified exhaust streams. The engine is at lean A/F all the time.

- 15 -

It should be noted that reductant injection need not occur for the full duration of the low-flow condition. Also reductant injection can occur at any time during the low-flow condition. Preferably, injection occurs
5 immediately after the adsorption means is switched to the low-flow condition. In this way, the adsorption means being regenerated is regenerated as soon as possible so that when reductant injection is ceased, the adsorption means will be able to adsorb any pollutants that are
10 present in the low-flow stream. Also, reductant injection may be provided a second time at a point in time to insure the adsorption means is fully regenerated before being switched to the high-flow adsorption condition.

15 Control Strategies

The following detailed discussions on control strategies is not intended to be limiting on the various strategies that one skilled in the art may be able to apply to the apparatus of the present invention.

20 The basic objective of any control strategy is to alternate the high-flow condition and the low-flow condition between the first and second adsorption means as explained above. Thus, when one of the adsorption means becomes saturated or near the pollutant breakthrough point (i.e., the point when the adsorbent is no longer capable of effectively adsorbing the pollutant before the pollutant exits into the atmosphere) in the
25 high-flow mode, a changeover is made so that the

- 16 -

regenerated absorption means receives the high-flow stream and the saturated absorption means receives the low-flow stream, preferably initially injected with reductant, to begin regeneration of the saturated adsorbent means. The changeover is repeated to effectively prevent the pollutant from entering the atmosphere.

Thus, the basic requirements of the control strategy are to effectively predict or monitor the condition (i.e., saturated or regenerated) of the adsorption means. To accomplish this, the following tasks are performed to determine (i) the quantity of the pollutant (NOx or Sox) adsorbed on the adsorption means; (ii) when to switch the adsorber between the high-flow and low-flow conditions; (iii) the amount of reductant to inject; and (iv) when to turn the reductant off.

Figure 3 depicts a basic control algorithm showing boxes (1) to (11) containing short descriptions of typical steps for controlling the apparatus of the present invention. The control algorithm will be explained below for an embodiment wherein two O₂ or A/F sensors are used downstream from the adsorption means. It will be appreciated by one skilled in-the-art that the following descriptions are illustrative and not intended to be limitative of other control strategies or sensors useful in controlling the apparatus of the present invention.

- 17 -

Oxygen Sensor or A/F Sensor Algorithm

Initialization Box (1) - This box performs the following functions when an engine is turned on:

- Check separator means (valve) flag - determines the valve position and assigns the two adsorption means as either the high-flow adsorber (e.g., Adsorber A) or the low-flow adsorber (e.g., Adsorber B). Valve position also determines the high-flow split fraction ("S") which is $0 < S < 1$.
- 5 ● Initialize the calculated quantity of adsorbed NOx ("gNOx") - First time the engine is run $gNOx^{An}=gNOx^{Bn}=0$, otherwise $gNOx^{An}$ and $gNOx^{Bn}$ are equal to values stored in memory from the previous time the engine was running. "n" is an iteration indicator which is an integer equal to 0 when first started.
- 10 ● Initialize timer - used in calculating amount of NOx produced from engine.
- 15 ● Initialize timer - used in calculating amount of NOx produced from engine.

Calculate Adsorbed NOx Box (2) - This box determines the amount of NOx adsorbed on Adsorbers A and B.

$$gNOx^{An+1} = gNOx^{An} + (\text{mass flow}) * (\text{EONOX}) * \eta * S * \text{time} \quad [1]$$

$$gNOx^{Bn+1} = gNOx^{Bn} + (\text{mass flow}) * (\text{EONOX}) * \eta * (1-S) * \text{time} \quad [2]$$

where:

- 25 $gNOx^{An+1}$ = amount of adsorbed NOx in Adsorber A
- $gNOx^{Bn+1}$ = amount of adsorbed NOx in Adsorber B
- $gNOx^{An}$ = amount of NOx adsorbed in Adsorber A initially or from prior iteration

- 18 -

gNOx^{Bn} = amount of NOx adsorbed in Adsorber B initially or from prior iteration
mass flow = engine mass flow obtained from mass air sensor
5 EONOX = engine out NOx mass rate obtained from data table in an automobile's ("ECU") as function of engine speed and load (i.e., engine mapping)
10 η = adsorption efficiency obtained from data table in the ECU as function of engine speed and load
S = high-flow split fraction, 0<S<1
time = time spent at speed and load

As these calculations are performed, the reductant
15 injection at Adsorber B is activated. We presume the existence of a "pumping means" to introduce the reductant (here presumed to be fuel). The amount of fuel, or flow rate, injected can be predetermined for a given gNOX, with the data stored in another data table of the ECU.
20 The reductant flow rate is injected until such time as the oxygen or A/F sensor detects that the stream exiting Adsorber B is going rich. (see Box 7) (The NOx that is adsorbed in Adsorber B acts as oxygen storage and so the downstream A/F will not become rich until all of this
25 oxygen storage is used up.) Then, the reductant injection is deactivated and Adsorber B is allowed to start adsorbing NOx in the low-flow condition.

- 19 -

Time to Regenerate? Box (3) - Check that adsorbed NOx does not exceed adsorption capacity of the high-flow adsorber by a check of the inequality:

$$gNOx^{An+1} < maxNOx * F_s \quad [3]$$

5 where:

maxNOx = maximum amount of adsorbed NOx before regeneration is required

F_s = safety factor to accommodate transient fluctuations and interpolation between data table entries (<1.0)

10

If equation [3] is true, Adsorber A is not filled to its adsorption capacity and it is not time to regenerate and a signal is sent to Engine Running? (Box (9)). If the engine is running, then an iteration is concluded and new values for equations [1] and [2] are calculated at Box 15 (2). If the engine is not running in Box (9), the engine is off, the values (settings) for $gNOx^{An+1}$, $gNOx^{Bn+1}$, and S are stored to be used as initial settings when the engine is turned back on. Once the settings are stored, the 20 algorithm is exited (END Box(11)).

If equation [3] is not true, Adsorber A is near adsorption capacity. A check is made to see if the engine is running- Box (4).

Engine Running? Box (4) - If the engine is off, the 25 settings are stored and the algorithm is exited as

- 20 -

explained above. (Boxes (10) and (11)). If the engine is still running, go to Box (5).

Switch Separator Flow/Inject Reductant Box (5) - When adsorption capacity is nearly full, i.e.,

5 $gNOx^{An+1} \geq maxNOx^*Fs$ [4]

a signal is sent to activate the flow separation means (valve) to direct the high-flow condition to Adsorber B and the low-flow condition to Adsorber A. The algorithm assigns $gNOx^{An+1} = gNOx^{Bn+1}$ and injects reductant based on 10 an injection rate from a data table. All other settings/values are also exchanged relating to Adsorber A and Adsorber B such that the designation Adsorber A will refer to the high-flow case.

15 Calculate High Flow Adsorbed NOx Box (6) - Based on the newly exchanged values from Box 5, the amount of NOx adsorbed in Adsorber A (high-flow) is calculated by equation [1].

Downstream O₂ / A/F Sensor Indicating HC Rich Condition?
Box(7) - If a hydrocarbon-rich condition is indicated, 20 the Adsorber B has been regenerated because reductant is breaking through and is no longer reducing NOx. Go to Box (8). If no reductant breakthrough detected, Adsorber B is not regenerated, go back to Box (6).

- 21 -

Turn Off Reductant/ Set gNOx^{Bn+1}=0 Box (8) - When this point is reached, Adsorber B has been regenerated. Reductant injection is turned off and the amount of adsorbed NOx in Adsorber B is set to 0. ($gNOx^{Bn+1}=0$). Go 5 back to Box (2) and repeat foregoing until engine turned off.

Engine Running? Boxes (4) and (9) - When engine is turned off, go to Box (10).

10 Store Settings Box 10 - If engine is turned off, current settings are stored until the engine is turned back on and become the initial settings for the new engine running period. Go to Box (11).

End Box (11) - End of algorithm.

NO_x Sensor Algorithm

15 This algorithm description also starts at the point where the separation means has been activated to direct the high-flow condition to Adsorber A to begin pollutant adsorption.

20 The algorithm for use with a NO_x sensor is the same as in Figure 3 and as described in the O₂ / A/F sensor algorithm. The following description highlights the major differences. According to this embodiment, there are two NO_x sensors and two O₂ sensors. Each type of sensor is placed downstream of Adsorber A and Adsorber B, 25 respectively.

- 22 -

Calculate Adsorbed NOx Box (2) - This calculation is based on an estimate of the efficiency of NOx absorption in the adsorbers using the equations:

$$\eta_{calc}^A = \{ (EONOx)(S) - (TPNOx)^A \} / (EONOx)(S) \quad [1']$$

$$5 \quad \eta_{calc}^B = \{ (EONOx)(1-S) - (TPNOx)^B \} / (EONOx)(1-S) \quad [2']$$

where:

η_{calc} = estimated efficiency of adsorbed NOx in indicated adsorber (A or B).

10 EONOx = engine out NO_x mass rate obtained from data table in ECU as function of engine speed and load.

S = high-flow split fraction (0 < S < 1).

15 TPNOx = tailpipe NOx mass rate obtained from NOx sensor at outlet of indicated adsorber (A or B).

Time to Regenerate? Box (3) - The decision to regenerate Adsorber A and switch the high-flow condition to Adsorber B is made by comparing Equation [1'] to a previously measured known efficiency that is stored in a data table 20 or equation in the ECU. For example, previously measured efficiencies, η_{EXP} , could be stored in a speed load table. Alternatively, temperature could be stored in a speed load table with an equation that relates efficiency as a function of temperature, i.e.

- 23 -

$$\eta_{EXP} = f(T) \quad [3']$$

Regardless of the method of data storage, the comparison is made for the condition:

$$\eta_{calc}^A < \eta_{EXP} \quad [4']$$

5 If equation [4'] is true, a regeneration is initiated.

Each time the engine operating condition changes, a new η_{EXP} value is obtained from the engine map and equations [1'] and [2'] are updated, and equation [4'] is checked. When equation [4'] is satisfied, a signal is sent to activate the flow separation means to direct the high-flow condition to Adsorber B and the low-flow condition to Adsorber A (i.e., go to Boxes (4) and (5) of algorithm). The algorithm as described before then reassigned the high-flow and low-flow functions such that Adsorber B is substituted for Adsorber A and Adsorber A is substituted for Adsorber B. In this way, Adsorber A will designate the high-flow condition adsorber and Adsorber B will designate the low-flow condition adsorber. All other algorithm steps are essentially the same as discussed for the O₂ / A/F flow sensor algorithm.

Simulation of Invention and Examples

Figure 4 illustrates a bench test apparatus used to simulate the invention by monitoring NOx conversion. All numbered elements are consistent with previous Figures 1

- 24 -

and 2. Figure 4 additionally depicts a cylinder 60 for supplying reductant and a solenoid valve 36 for controlling the amount of reductant. Also NOx sensor 47 was added to measure the concentration of NOx entering 5 adsorption means 40. In essence, Figure 4 represents one side of this invention's pollutant concentration apparatus.

The type of engine used for the simulation was 8 cylinder, 4.6L engine. The adsorbent material used was 10 SrO homogeneously mixed with catalyst of Pt/Rh on Al₂O₃. The operating condition of engine 10 was set to 2000 rpm at 16 in Hg vacuum. This gives a total exhaust flow of 42.9 SCFM. The A/F ratio of the engine was fixed at $\lambda = 1.28$. Separation means 20 was set so that in the "ON" (high-flow 15 condition), $\frac{1}{4}$ of flow 15 was directed to the adsorbent means and $\frac{3}{4}$ was directed to the vent system. Under the high-flow condition, adsorption of NOx occurs. In the "OFF" position (low-flow condition), the separator means 20 was adjusted so that $\frac{1}{8}$ of flow 15 was directed to 20 the adsorption means and $\frac{7}{8}$ of flow 15 was directed to the vent system. This simulates the system of the invention with a 4/1 flow split, i.e., having $\frac{1}{4}$ (25%) of flow 15 for regeneration flow. The reductant was delivered to the adsorption means during the low-flow 25 period. The correct injection flow was adjusted by measuring the A/F ratio. Gas concentration of CO, O₂, HC and NOx were measured using the following conventional analyzers:

- 25 -

Carbon Monoxide	-	Rosemount Model 880 Nondispersive Infrared Analyzer
Hydrocarbon	-	Beckman Model 400A Flame Ionization Detector Analyzer
5 Oxygen	-	Beckman Model OM1EA Paramagnetic Analyzer
Nitrogen Oxides	-	Rosemount Model 951A Chemiluminescent Analyzer

These measurements were used to calculate the A/F ratio
10 as described in SAE 770365 in front of the adsorption means during the steady state low-flow condition. The target A/F ratio produced $\lambda \approx 0.9$ at the adsorption means inlet. Solenoid valve 36 was used to initiate and terminate the reductant flow. Pure carbon monoxide
15 ($>99.5\%$) and pure propylene ($>99.0\%$) were supplied from cylinders for the simulation. The actual invention may employ injecting gasoline or diesel fuel as reductant depending on the application. In other applications, reductants including natural gas, urea, ammonia, cracked
20 hydrocarbon gas and diesel could be used. The experiment was programmed in a manner which allowed variable injection time.

Comparative Example, C-1:

The adsorption means was regenerated with a flow of
25 rich exhaust gas by injecting reductant during the low-flow condition. The separator means 20 was switched to the high-flow condition with the engine continuously operated at $\lambda \approx 1.28$. The NO_x concentration was monitored at the inlet and exit of the adsorption means

- 26 -

by the above-described analyzers. The "NOx Conversion" as a function of time is shown in Figure 5. "NOx Conversion" is defined as follows:

$$5 \quad \text{NOx Conversion} = \frac{[\text{NOx}]_{\text{in}} - [\text{NOx}]_{\text{out}}}{[\text{NOx}]_{\text{in}}} \times 100$$

As shown in Figure 5, the NOx conversion is very high initially. As the trapping agent fills up, however, the performance degrades very quickly and, after about three 10 minutes, falls precipitously toward zero.

Comparative Example, C-2:

The NOx trap was run in a "Partial Lean Burn" mode. At the start of the experiment, the engine was set at 2000 rpm and 16 inches Hg vacuum with separator means 20 15 set to give $\frac{1}{2}$ the total flow. Initially, the engine A/F ratio was set at the stoichiometric point $\lambda = 1$.

The engine A/F ratio was controlled to cycle between $\lambda \approx 1.3$ and $\lambda \approx 0.9$ with the lean cycle increased from 10 sec to 60 sec, to 90 sec, and finally to 120 sec and the 20 rich cycle was maintained always at 15 sec. The results are shown in Figure 6. It can be seen that the NOx conversion remains high throughout the test. The cost of obtaining that performance is in the fuel required to reduce the A/F ratio in the engine to $\lambda \approx 0.9$.

- 27 -

Inventive Example, I-1:

The invention was simulated with a 29 second injection of carbon monoxide initiated at the low-flow changeover. The adsorption means was exposed to 60 seconds of high-flow and then the diverter valve was switched to the low-flow condition. At 31 seconds into the low-flow condition, the carbon monoxide injection was initiated for 29 seconds. Then the carbon monoxide injection was terminated and the diverter valve switched to the high-flow condition. This cycle was repeated continuously for approximately 20 minutes. A segment of the test is shown in Figure 7.

Inventive Example, I-2:

The invention was simulated as in example I-1, but 15 with only a 10 second injection of carbon monoxide. The cycle was repeated for over 15 minutes. A segment of the test is shown in Figure 8.

Inventive Example, I-3:

The invention was simulated as in example I-2, but 20 with a 10 second injection of propylene. Because of a limitation in measuring high hydrocarbon concentration at the inlet of the adsorption means, the A/F ratio at the adsorption means inlet was only $\lambda = 0.99$. The test cycle was repeated continuously for over 15 minutes. A segment 25 of the test is shown in Figure 9. During the regeneration period, there was insufficient reductant

available at $\lambda = 0.99$ so NOx is not completely reduced to N₂.

Inventive Example, I-4:

The invention was simulated as in example I-3, but 5 with the A/F ratio at the adsorption means decreased to $\lambda \approx 0.90$. A segment of the test is shown in Figure 10. Referring to Figure 10, it is quite apparent that consistent NOx conversion is achieved throughout the test. NOx conversion does not decrease below 80% in 10 contrast to the previous experiments. Also, the average NOx conversion for the test is approximately 94.2%. This is quite an accomplishment for an engine running at $\lambda \approx 1.3$.

In considering the teachings of Inventive Examples, 15 I-1 to I-4, it is apparent that with the proper choice and amount of reductant, extremely high NOx conversion rates upwards of 90 percent and higher are achievable under engine operating conditions (i.e., lean operating conditions) corresponding to $\lambda \approx 1.3$. For example, 20 example I-2 shows that a 10 second CO pulse does not fully regenerate the adsorption means and therefore a sharp reduction in NOx conversion is observed when compared with example I-1. Example I-3 shows that with propylene as reductant, the adsorbent means regenerates 25 but there is insufficient reductant to reduce the NOx as NOx breakthrough spikes are observed during the time when reductant is added. Example I-4 shows sufficient

reductant is supplied to regenerate and reduce the NOx as there are no observed NOx breakthrough spikes during the reductant injection phase.

In comparing Comparative Example, C-2 to Inventive Example, I-4, it is observed that example I-4 gives comparable NOx conversion (> 90%). However, example I-4 is able to provide this performance with a substantially lower consumption of reductant. Specifically, based on 10 second reductant injection periods, example C-2 requires approximately 8.06 grams of reductant to achieve approximately 98% NOx conversion while example I-2 only requires approximately 2.02 grams of reductant to achieve approximately 94% NOx conversion. Thus, only approximately 25% of the reductant used in example C-2 is needed in example I-4 to achieve a comparable NOx conversion.

Furthermore, it has been observed that regeneration of the adsorption means should occur shortly after switched to the low-flow condition. In this way, the adsorption means can be regenerated and ready to switch to the high-flow adsorption mode as required. Otherwise, injection at a time distant from the low-flow mode (regeneration) changeover complicates the control as anticipation of the drive cycle is required.

While specific embodiments of the present invention are described in detail herein, they are illustrative in nature, and the scope of the present invention is defined in the claims that follow. Modifications to the illustrated embodiments will occur to those skilled in

- 30 -

the art upon a reading of the accompanying disclosure.
Such modifications are also intended to be included
within the scope of the accompanying claims.

- 31 -

What is claimed is:

1. An apparatus for the concentration of adsorbable pollutants contained in gaseous streams comprising:
 - (a) an inlet conduit for receiving gases;
 - (b) means for separating and controlling the gases from said inlet conduit between at least a first conduit and a second conduit;
 - (c) a first pollutant adsorption means in fluid communication with said first conduit, said first means having inlet and outlet conduits; and
 - (d) a second pollutant adsorption means in fluid communication with said second conduit, said second means having inlet and outlet conduits.
2. The apparatus of claim 1, wherein the pollutant adsorption means further comprises means to inject a reductant.
3. The apparatus of claim 1, further comprising a heating source capable of heating the adsorption means to temperatures sufficient to adsorb and desorb adsorbed pollutants.
4. The apparatus of claim 1, wherein the adsorbent is selected from the group consisting of metal oxides, metal hydroxides, and mixed metal oxides.

- 32 -

5. The apparatus of claim 4, wherein the metal is selected from the group consisting of Group IA and Group IIA metals, lanthanum and manganese.

6. The apparatus of claim 4, wherein the adsorbent is selected from the group consisting of SrO, BaO, CaO, BaTiO₃, BaZrO₃, LaZrO₂, MnO₂, LaMnO_{x'}, and mixtures of La₂O₃ and CeO₂ with TiO₂ and ZrO₂ and where x' is an integer from 2 to 4.

7. The apparatus of claim 4, wherein the adsorbent is strontium oxide, barium oxide, or mixtures thereof.

8. The apparatus of claim 7, wherein the adsorbent contains an absorbency enhancing effective amount of platinum.

9. The apparatus of claim 4, wherein the adsorption means further comprises a catalytic effective amounts of metal selected from the group consisting of Pt, Pd, and Rh, and mixtures thereof.

10. The apparatus of claim 9, where the catalyst is selected from the group of mixtures of Pt and Rh and mixtures of Pt, Rh and Pd.

11. The apparatus of claim 9, wherein position of the catalyst relative to the adsorbent is an overlayer, as an underlayer, as separately provided behind the

- 33 -

adsorbent, or as a homogeneous mixture of adsorbent and catalyst.

12. The apparatus of claim 1 used in treating gaseous streams emanating from gasoline or diesel engines.

13. A method for concentration of adsorbable pollutants comprising the steps of:

- (a) receiving an adsorbable pollutant-containing gaseous stream;
- (b) providing means for separating said gaseous stream between at least a first stream and a second stream;
- (c) flowing said first stream into a first pollutant adsorption means;
- (d) flowing said second stream into a second pollutant adsorption means;
- (e) adsorbing the pollutant from said first stream in said first adsorption means and permitting said stream to exit said adsorption means;
- (f) regenerating said second adsorption means by desorbing adsorbed pollutant to form a concentrated pollutant-containing stream and permitting said stream to exit said adsorption means; and
- (g) periodically cycling the adsorption and regeneration functions of steps (e) and (f) between said first and second adsorption means.

- 34 -

14. The method of claim 13, wherein the pollutants are oxides of nitrogen or sulfur.

15. A system for concentration of adsorbable pollutants comprising:

(a) an engine which generates an adsorbable pollutant-containing gas;

(b) means for separating the gas into at least a first stream and a second stream;

(c) means for receiving said first stream into a first means for adsorbable pollutant adsorption;

(d) means for receiving said second stream into a second means for adsorbable pollutant adsorption;

(e) adsorbing the pollutant from said first stream in said first adsorption means and permitting said stream to exit said adsorption means;

(f) regenerating said second adsorption means by desorbing adsorbed pollutant to form a concentrated pollutant-containing stream and permitting said stream to exit said adsorption means; and

(g) periodically cycling the adsorption and regeneration functions of steps (e) and (f) between said first and second adsorption means.

16. The system of claim 15, wherein the pollutants are oxides of nitrogen or sulfur.

17. A control strategy for concentrating adsorbable pollutants in a system having at least two separate and

- 35 -

parallel adsorption means where when one of the adsorption means is in a high-flow adsorption mode the other adsorption means is in a low-flow concentration mode, comprising the steps of:

- (a) estimating the amount of pollutant adsorbed in the high-flow adsorption means;
- (b) determining when the high-flow adsorption means is near to its adsorption capacity;
- (c) if the high-flow adsorber capacity is not full, repeating steps (a) and (b);
- (d) if the high-flow adsorption means is near to its adsorption capacity, switching the low-flow adsorber to the high-flow mode and the high-flow adsorber to the low-flow mode;
- (e) activating means to desorb and concentrate the pollutant in the low-flow adsorber;
- (f) repeating steps (a) to (e) until the system is turned off.

18. The strategy of claim 17, wherein the estimated amount of adsorbed pollutant is stored when the system is turned off and used as the estimated amount when the system is turned on again.

19. The strategy of claim 17, wherein the means to desorb and concentrate the pollutant is deactivated.

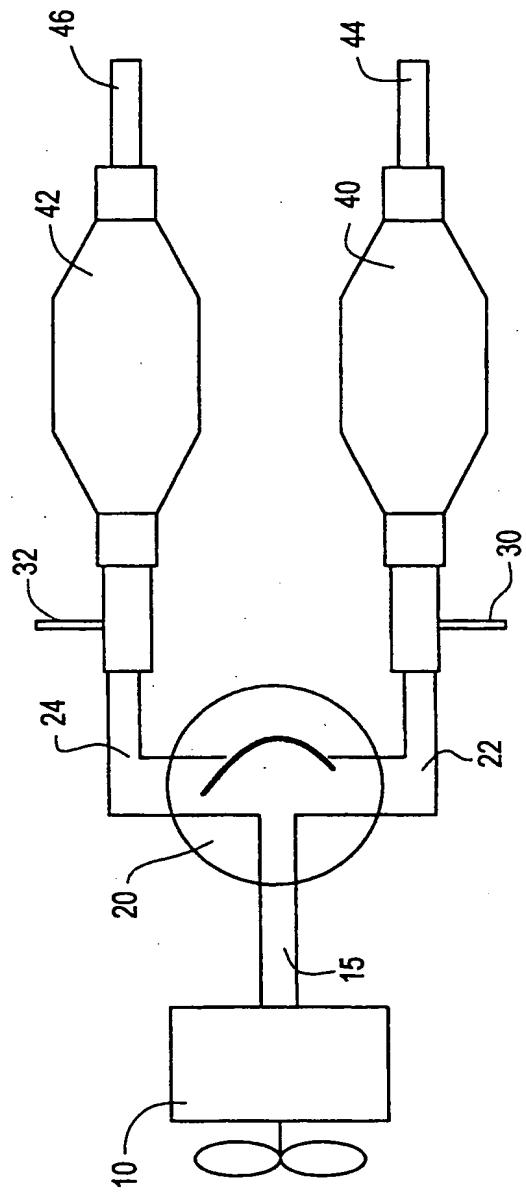
20. The strategy of claim 19, wherein the means to desorb and concentrate the pollutant is deactivated based

- 36 -

on a timer, or detection of a reductant-rich condition by an oxygen sensor downstream of the low-flow adsorber.

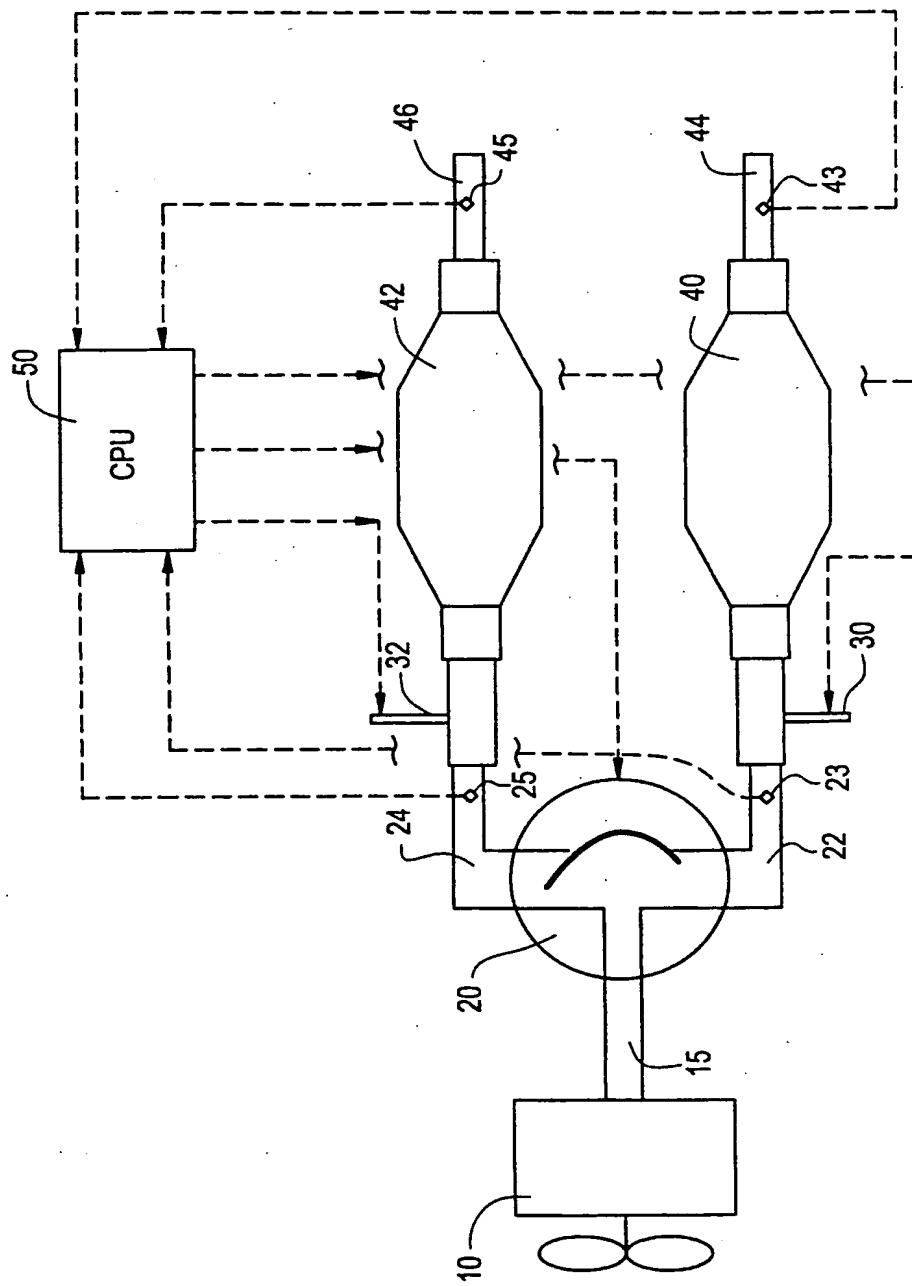
1 / 10

FIG. 1



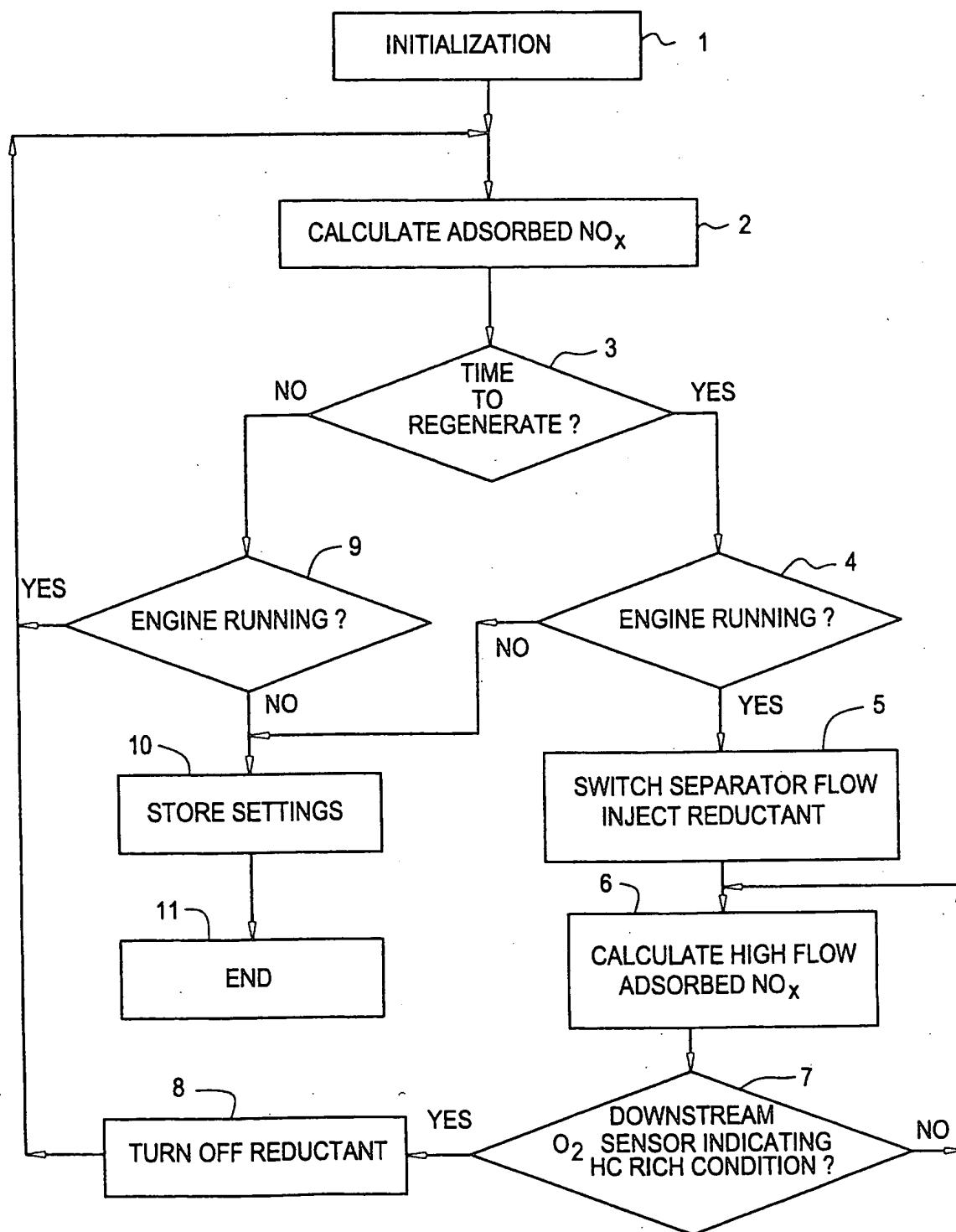
2 / 10

FIG. 2



3 / 10

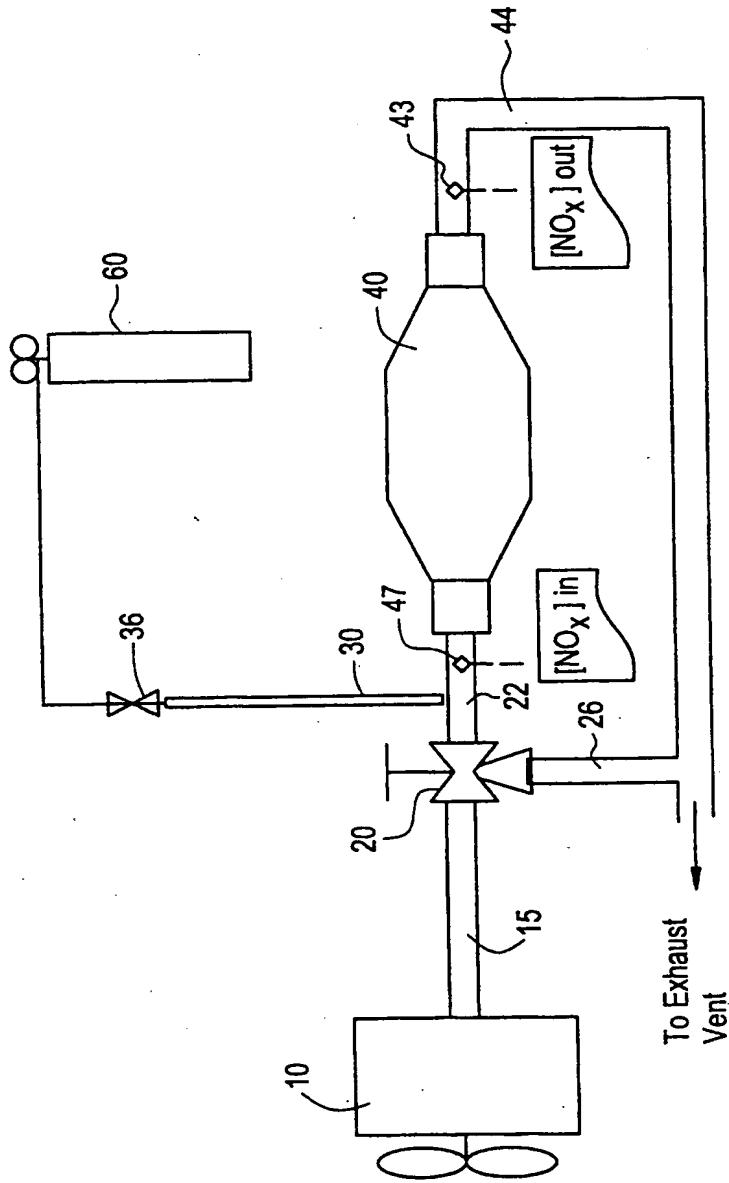
FIG. 3



SUBSTITUTE SHEET (RULE 26)

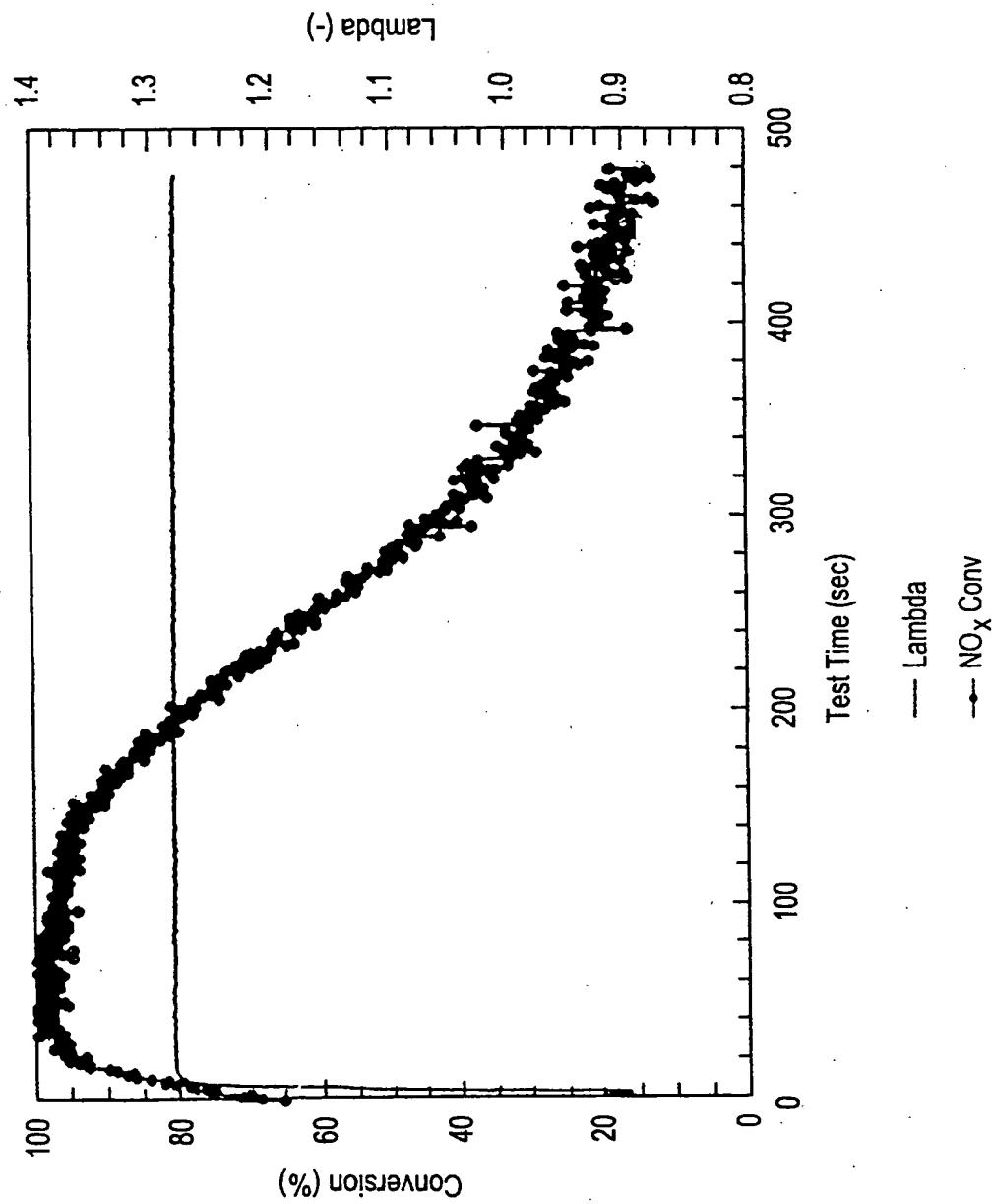
4 / 10

FIG. 4



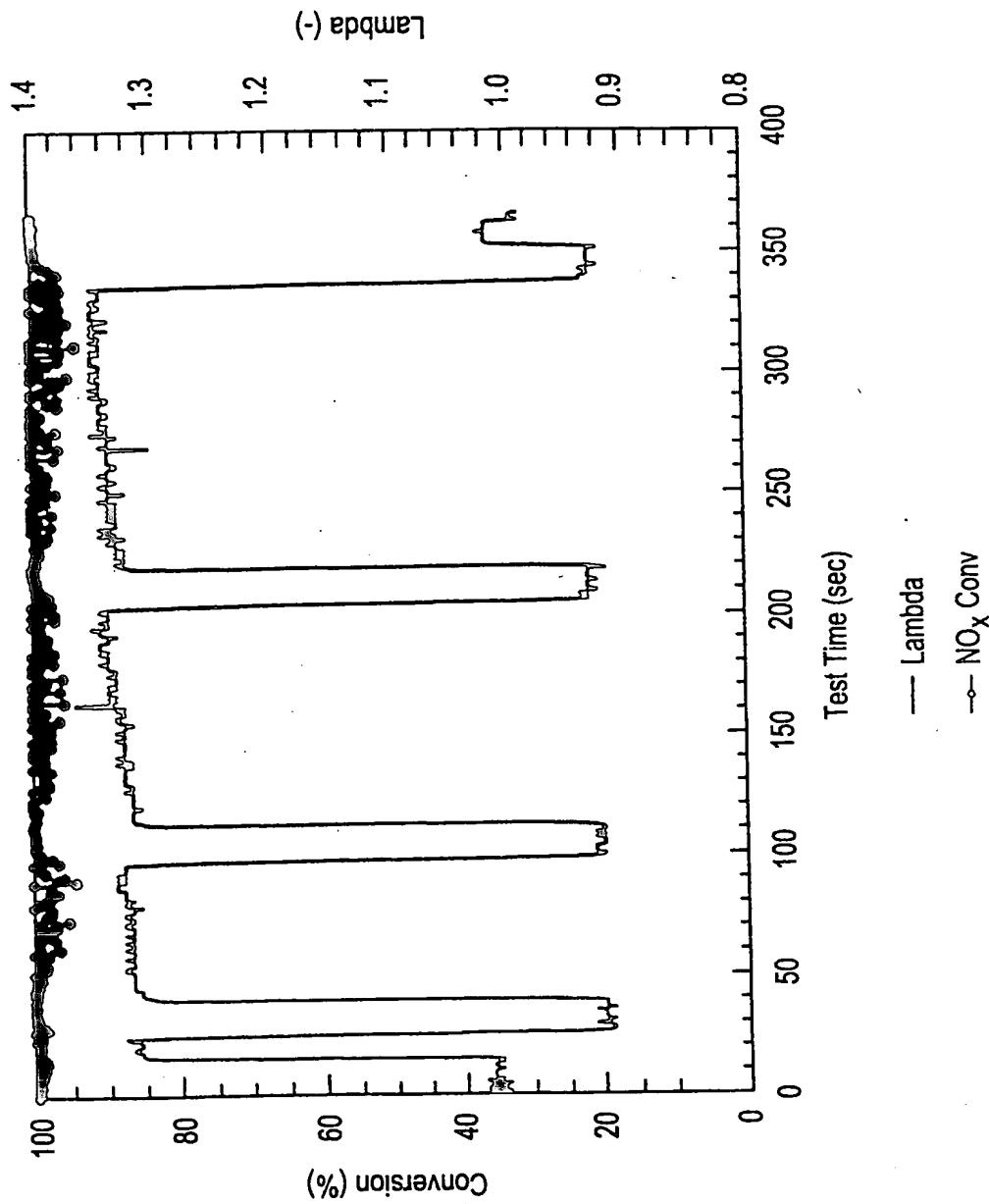
5 / 10

FIG. 5



6 / 10

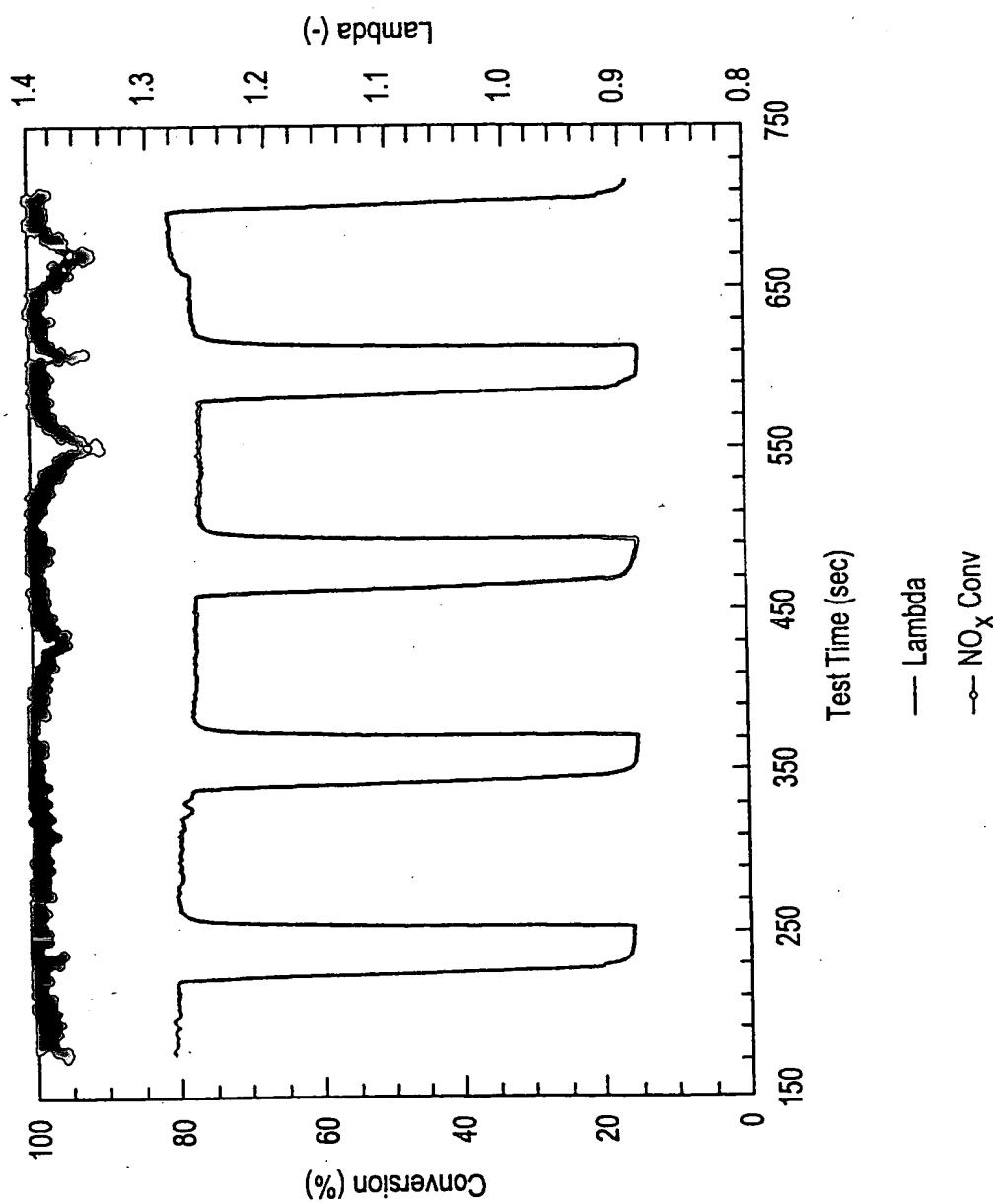
FIG. 6



SUBSTITUTE SHEET (RULE 26)

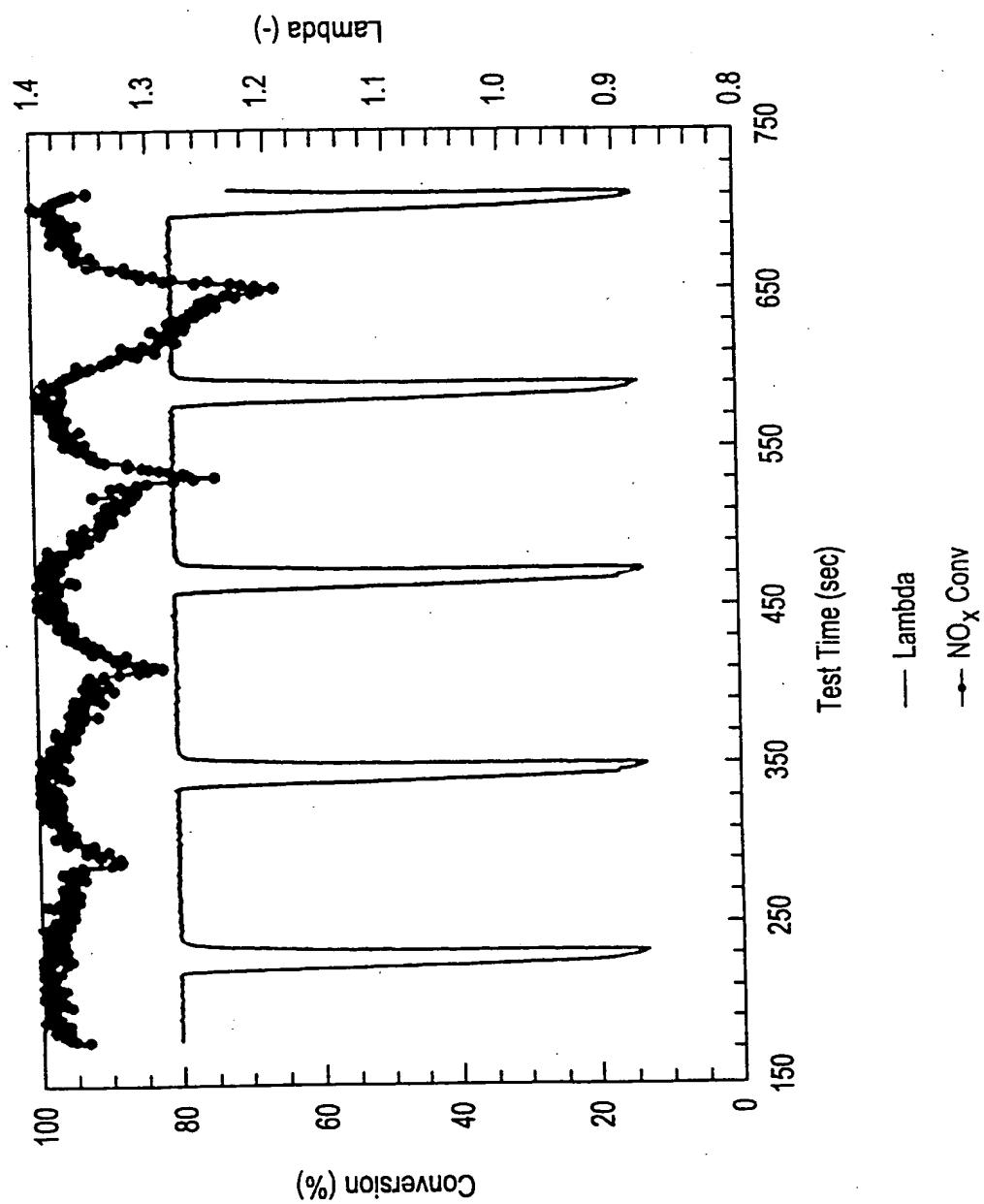
2 / 10

FIG. 7



8 / 10

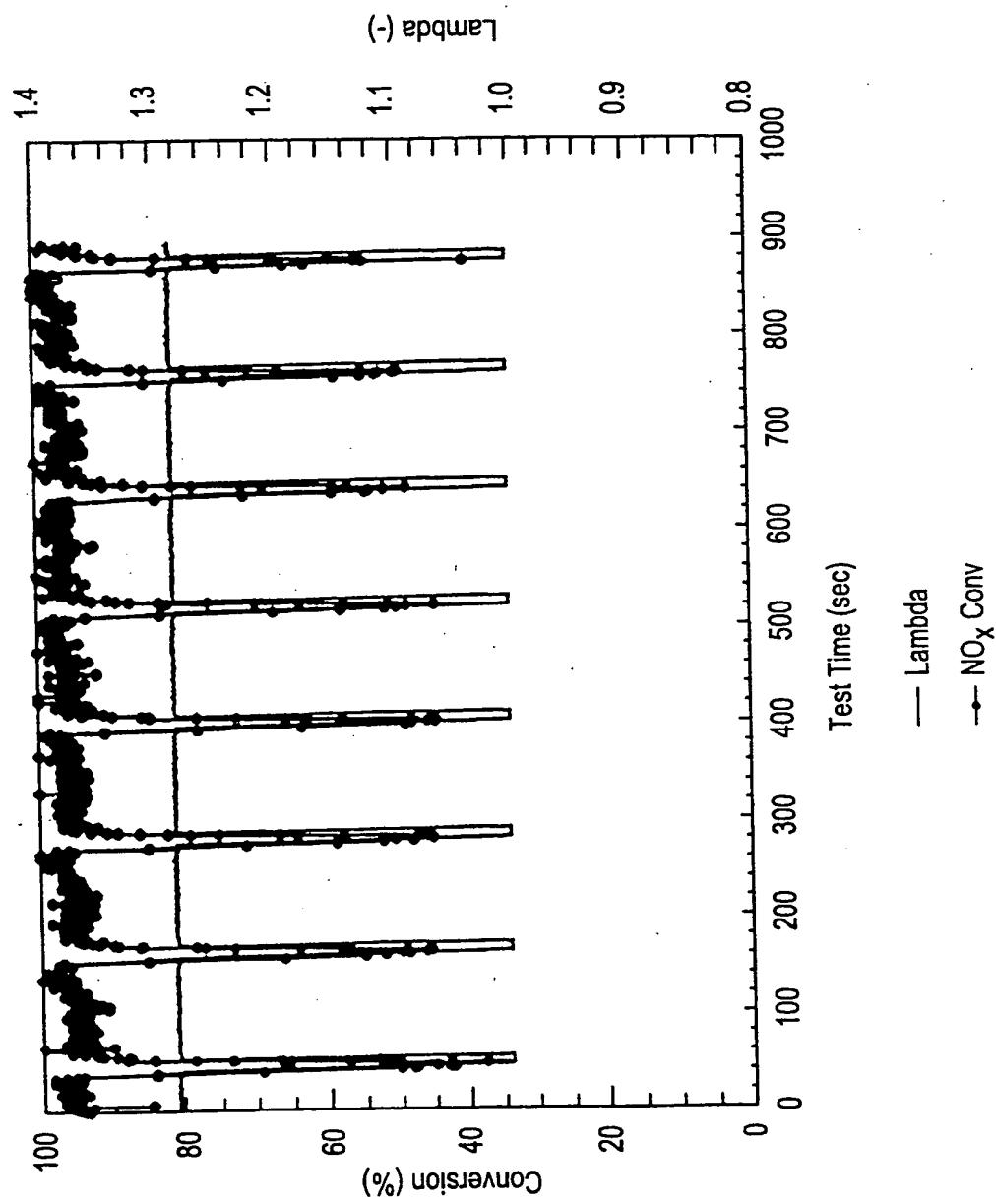
FIG. 8



SUBSTITUTE SHEET (RULE 26)

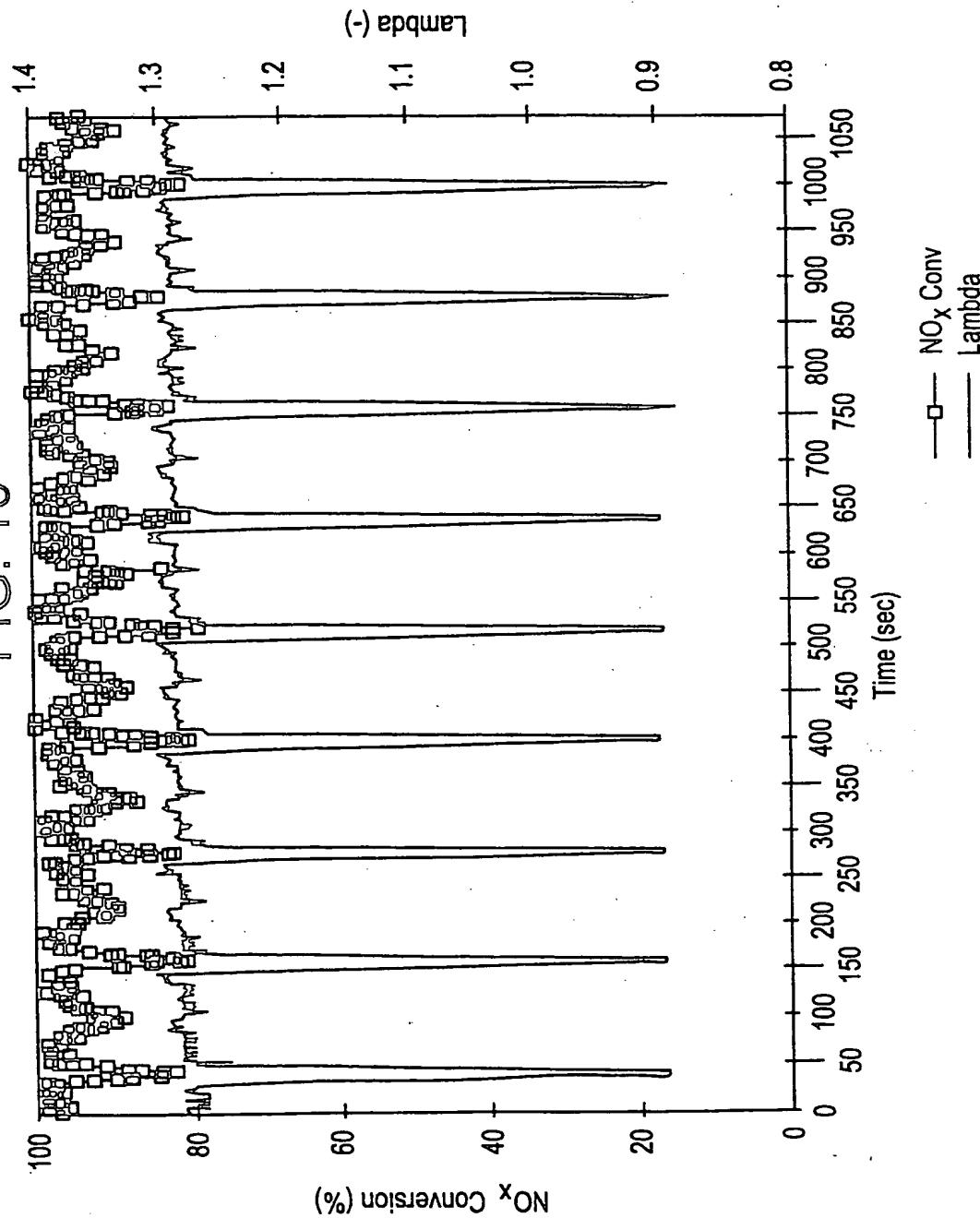
9 / 10

FIG. 9



10 / 10

FIG. 10



SUBSTITUTE SHEET (RULE 26)

INTERNATIONAL SEARCH REPORT

Int'l. Application No
PCT/US 98/05536

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 F01N3/08 B01D53/94

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 F01N B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DE 43 42 062 A (TOYOTA MOTOR CO LTD) 16 June 1994</p> <p>see column 1, line 66 - column 2, line 19 see column 4, line 43 - column 10, line 21 see column 10, line 58 - column 11, line 7 see column 16, line 12 - column 20, line 52; figures 3-8,15</p> <p>---</p> <p>EP 0 702 134 A (TOYOTA MOTOR CO LTD) 20 March 1996</p> <p>see column 2, line 16 - column 4, line 28 see column 5, line 3 - column 13, line 12 see column 15, line 14 - line 46; figures 1-4,6</p> <p>---</p> <p>---</p>	<p>1,2, 5-12,17, 19,20</p> <p>1,2,4-12</p>
		-/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

9 July 1998

Date of mailing of the international search report

17/07/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
 Fax: (+31-70) 340-3016

Authorized officer

Cubas Alcaraz, J

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/05536

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 540 280 A (TOYOTA MOTOR CO LTD) 5 May 1993 see the whole document	1,3-8,12
X	DE 196 26 836 A (VOLKSWAGENWERK AG) 9 January 1997 see page 5 - page 7; figures 1-6	1-3,12
A	EP 0 562 805 A (TOYOTA JIDOSHA KABUSHIKI KAISHA) 29 September 1993 see column 1, line 41 - column 2, line 55 see column 11, line 1 - column 12, line 50; claims 1-12; figures 1,14 & US 5 365 734 A cited in the application	1-20
A	EP 0 718 476 A (TOYOTA MOTOR CO LTD) 26 June 1996 see the whole document	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte ~~l~~ ~~onal~~ Application No
PCT/US 98/05536

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
DE 4342062 A	16-06-1994	JP	6173654 A	21-06-1994
		JP	6200738 A	19-07-1994
		US	5406790 A	18-04-1995
EP 0702134 A	20-03-1996	JP	8086213 A	02-04-1996
EP 0540280 A	05-05-1993	JP	5195755 A	03-08-1993
		DE	69205389 D	16-11-1995
		DE	69205389 T	04-04-1996
		US	5388406 A	14-02-1995
DE 19626836 A	09-01-1997	DE	19626835 A	09-01-1997
		DE	19626837 A	09-01-1997
EP 562805 A	29-09-1993	JP	5272332 A	19-10-1993
		JP	5272330 A	19-10-1993
		JP	5288042 A	02-11-1993
		DE	69300645 D	23-11-1995
		DE	69300645 T	11-04-1996
		US	5365734 A	22-11-1994
EP 0718476 A	26-06-1996	JP	8177525 A	09-07-1996
		US	5697211 A	16-12-1997